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SOME PROPERTIES OF SINGLE METAL CRYSTALS

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In this note I summarize the results of measurements of a number of the physical properties of single crystals of the more readily obtainable non-cubic metals, Zn, Cd, Bi, Sb, Te, and Sn. The detailed description of the measurements and the method of producing the crystals is to be given elsewhere (probably in *Proc. Amer. Acad. Arts Sci., Boston*). I also give a few measurements on a single crystal of tungsten (cubic system) which I owe to the courtesy of Dr. Langmuir of the General Electric Co. who obtained it from a German firm. The measurements given here include the elastic constants at room temperature, the linear compressibilities at 30° and 75° C. to 12,000 kg./cm.^{2}, the thermal expansion, the specific electrical resistance, the temperature coefficient of resistance, and the effect of pressure on resistance to 12,000 kg. at several temperatures.

All of the metals in the list above are characterized by an axis of rotational symmetry; Zn and Cd have a six-fold axis (hexagonal system), Bi, Sb, and Te a three-fold axis (trigonal system), and Sn a four-fold axis (tetragonal system). The rotational axis is taken as the datum line in the crystal; when, for example, a property is specified in the perpendicular direction, the direction perpendicular to the axis is understood. Besides the principal axis, there are principal planes. Zn, Bi, and Sb show perfect cleavage on a single plane perpendicular to the axis, Cd and Sn have no cleavage but the most important slip plane is also perpendicular to the axis, while Te, on the other hand, has three principal cleavage planes, intersecting in three lines parallel to the principal axis.

Of the properties above, the elastic constants are the most complicated; the trigonal and tetragonal systems have six independent constants, and the hexagonal system five. The notation of Voigt for the elastic constants is used in the following. All the other properties have rotational symmetry, so that the linear compressibility or thermal expansion or electrical

resistance is completely determined for all directions in the crystal if it is determined parallel and perpendicular to the axis.

There follows now the numerical summary.

ELASTIC CONSTANTS IN ABS. C. G. S. UNITS

CONSTANT	ZN	CD	BI	SB	TE	SN	W
s_{11}	8.23×10^{-13}	12.9×10^{-13}	26.9×10^{-13}	17.7×10^{-13}	48.7×10^{-13}	18.5×10^{-13}	2.534×10^{-13}
s_{12}	+ .34	−1.5	−14.0	−3.8	−6.9	−9.9	−.726
s_{13}	−6.64	−9.3	−6.2	−8.5	−13.8	−2.5	s_{12}
s_{33}	26.38	36.9	28.7	33.8	23.4	11.8	s_{11}
s_{44}	25.0	64.0	104.8	41.0	58.1	57.0	6.55
s_{66}	$2(s_{11} - s_{12})$	$2(s_{11} - s_{12})$	$2(s_{11} - s_{12})$	$2(s_{11} - s_{12})$	$2(s_{11} - s_{12})$	135.	$2(s_{11} - s_{12})$
s_{14}	0	0	+16.0	−8.0	Not determined	0	0

LINEAR COMPRESSIBILITY, $\left(\frac{\Delta l}{l_0}\right)$

Pressure in kg./cm.^{2} Range, 12,000 kg./cm.^{2}

METAL		AT 30° C.	AT 75° C.
Zn	∥	$12.98 \times 10^{-7}p - 5.32 \times 10^{-12}p^2$	$13.55 \times 10^{-7}p - 7.82 \times 10^{-12}p^2$
	⊥	$1.946 - 1.11$	$2.025 - 1.47$
Bi	∥	$15.92 - 11.1$	$15.80 - 11.6$
	⊥	$6.450 - 4.60$	$6.423 - 4.57$
Sb	∥	$16.48 - 20.5$	$16.37 - 18.0$
	⊥	$5.256 - 4.56$	$5.091 - 3.04$
Te	∥	$-4.137 + 9.6$	$-5.132 + 13.2$
	⊥	$27.48 - 52.7$	$27.77 - 53.6$
Sn	∥	$6.719 - 4.07$	$6.956 - 3.91$
	⊥	$6.022 - 4.20$	$6.144 - 4.26$

From the directly measured linear compressibility the cubic compressibilities may be calculated.

CUBIC COMPRESSIBILITY, $\left(\frac{\Delta V}{V_0}\right)$

Pressure in kg./cm.^{2} Range, 12,000 kg./cm.^{2}

METAL	AT 30° C.	AT 75° C.
Zn	$16.87 \times 10^{-7}p - 8.08 \times 10^{-12}p^2$	$17.60 \times 10^{-7}p - 11.35 \times 10^{-12}p^2$
Bi	$29.17 - 22.43$	$29.89 - 31.13$
Sb	$26.99 - 31.6$	$26.55 - 25.3$
Te	$50.82 - 101.1$	$50.41 - 85.6$
Sn	$18.76 - 13.6$	$19.24 - 13.7$
W	$3.18 - 1.4$	$3.18 - 1.5$

LINEAR THERMAL EXPANSION AT ROOM TEMPERATURE

METAL	PARALLEL	PERPENDICULAR
Zn	57.4×10^{-6}	12.6×10^{-6}
Cd*	52.5	20.2
Bi	13.96	10.36
Sb	15.56	7.96
Te	— 1.6	27.2
Sn	30.50	15.45

* Values for Cd from E. Grüneisen and E. Goens, *Phys. Z.*, **24**, 506–510, 1923.

ELECTRICAL RESISTANCE

METAL		SP. RESISTANCE AT 20° C.	AVERAGE TEMPERATURE COEFF. OF SP. RESISTANCE 0–100° C.	INITIAL PRESSURE COEFF. OF SP. RESISTANCE AT 0° C.
Zn	∥	6.13×10^{-6}	.00419	-10.87×10^{-6}
	⊥	5.91	418	— 6.55
Cd	∥	8.30	428 (?)	—13.1
	⊥	6.80		— 8.7
Bi	∥	13.8	445	+24.5
	⊥	10.9	445	+ 7.5
Sb	∥	35.6	595	+17.2
	⊥	42.6	511	+ 1.05
Te	∥	56,000		
	⊥	154,000		
Sn	∥	14.3	447	—10.96
	⊥	9.9	469	—10.28
W		5.48		

The elastic constants are seen to vary greatly with direction, so that these single crystals do not by any means approach the behavior of isotropic bodies. The linear compressibility of Zn is nearly 7 times greater parallel to the axis than at right angles, and the linear compressibility of Te is *negative* parallel to the axis. The effective Young's moduli (s_{11} and s_{33}) also vary greatly with direction, although not so much as the linear compressibilities. Notice that in all cases the deformability is greatest across the principal cleavage or slip plane, except in the case of the effective Young's modulus of Sn. Since the separation of atomic centers is greatest across the cleavage or slip planes, we should expect in general a greater deformability in this direction.

Successful measurements of the compressibility of Cd were not obtained, owing to the existence of two new polymorphic forms under pressure. The transitions are reversible, and at 20° C. take place at about 3000 and 6000 kg./cm.^{2} In addition to changes of dimensions there is also a very slight change in the electrical resistance at the transition. The average in all directions in the crystal of the properties of the new modifications is very close indeed to those of the ordinary modification,

which explains why these modifications have escaped me in previous measurements on crystalline aggregates of Cd.

The thermal expansion is also in all cases greatest across the cleavage or slip planes. Notice the negative expansion of Te along the axis. It is interesting that the variation with direction of the elastic constants and thermal expansion is much greater in Zn and Cd than in Bi and Sb, which by ordinary standards have a much more strongly developed crystalline character. For the sake of completeness I have included in the table of thermal expansions the recent values of Grüneisen and Goens for Cd, who have also given values for all the other properties of Zn and Cd listed here, except the behavior under pressure. The samples of Cd which I had intended for these measurements were ruined by an exposure to pressure, which produced a disorientation on crossing the transitions points.

The differences of electrical conductivity in different directions are much less pronounced than the differences of elastic deformability, but follow the same general rule, namely the resistance is greatest *across* the plane of easiest cleavage or slip, that is, in the direction in which the atoms are most separated. The only exception to this rule is Sb. The temperature coefficient of resistance does not vary greatly with direction; the pressure coefficient varies much more. The resistance of Zn, Cd, and Sn decreases under pressure; the decrease is greatest parallel to the axis, that is, in the direction in which the atoms are brought closest together by pressure. Under high pressure the variations of resistance with direction become less accentuated for these three metals. Bi, on the other hand, increases in resistance under pressure, and the increase is more rapid parallel to the axis, so that the variation of resistance with direction becomes accentuated under pressure. The behavior of the resistance of Sb under pressure is very unusual and striking. Briefly, the effect of pressure is to compel a return to the normal type of behavior, so that under 12,000 kg. the resistance is greatest across the cleavage planes, as is normal. The return to normality is most rapid at the higher temperatures. The details of the pressure effect are complicated. (In the detailed paper, the resistance of all these metals is given as a function of pressure to 12,000 kg. and between 0° and 95° C.; the results are too complicated to be summarized here.) At the higher temperatures the sign of the pressure coefficient in the perpendicular direction reverses, and there are intermediate temperatures where the resistance passes through a maximum with increasing pressure, the only example known of such an effect. After pressure has compelled a return to normality, the effect of further increasing pressure is to accentuate still further the greater resistance across the cleavage planes. The fact that ultimately the preponderance of resistance across the cleavage planes of both Bi and Sb becomes accentuated as the atoms are brought closer together shows that the resistance is determined by

something more specific than the mere distance apart of the atoms, and that without doubt the details of atomic structure are involved.

I am indebted to my assistant, Mr. W. Koenig, for many of the readings on which these results are based.

EFFECT OF INSULIN ON THE LACTIC FERMENTATION

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August 28, 1924

A difficulty which seriously retards the progress of experimental investigations on insulin, as well as its preparation for clinical use, is that of determining even relatively the quantity present in solutions containing it. This research on its effect on the lactic fermentation was undertaken in the hope of developing a more satisfactory assay of insulin preparations than the animal-testing method affords. It was also thought that any effects observed might throw light on the mechanism of its physiological action. The research seemed promising since preliminary experiments had shown that addition of insulin considerably increased the total acid produced by the lactic fermentation as brought about by the organism Lactobacillus bulgaricus.

This research was made possible by a grant from the Carnegie Corporation of New York. We are also indebted to Eli Lilly and Company of Indianapolis for a supply of their purest insulin, to the Vitalait Laboratory of Pasadena for furnishing pure cultures of the lactic bacteria, to Miss Emma B. Mundy and Mr. John R. Adams of the Pasadena High School for bacteriological assistance, and to Messrs. G. A. Alles and A. L. Raymond of this Institute for valuable suggestions and for aid in preparing and testing the insulin preparations.

The fermentation experiments were made with mixtures that contained in 100 cc. of solution, 1 g. of glucose, 10 cc. of skimmed milk, 2 drops of a milk culture of Lactobacillus bulgaricus and varying amounts of insulin solution (or of a blank solution). The solutions were made up in glass-stoppered bottles, which were placed in a water thermostat at 32°, and which were either rotated on a horizontal shaft within the thermostat, or shaken by hand at fifteen-minute intervals for the first four hours and then occasionally till the solutions coagulated.

Two insulin samples were used, both of which were prepared from a highly concentrated aqueous solution furnished by Eli Lilly and Company. One (here called no. 1) was the precipitate obtained by adding a large

quantity of 95% ethyl alcohol; and the other (no. 2) by precipitating the alcoholic filtrate from this precipitate with ether. Both precipitates were impalpable powders, containing about 14% of nitrogen; no. 1 was light brown, and no. 2 almost snow-white.

The insulin activity of each sample was determined by finding the weight of it required, per kilo of rabbit weight, to produce in a majority of the large number of rabbits tested, the characteristic convulsions resulting from disappearance of the blood sugar; rabbits being used which had fasted for 16 to 24 hours before the tests, and which showed 110 to 120 mg. of glucose per 100 cc. of blood. The weights of samples no. 1 and no. 2 which produced this effect were found to be 0.10 mg. and 0.05 mg., respectively. Hence in sample no. 2 only half as much impurity was associated with a given quantity of insulin as in no. 1. The quantity added to 100 cc. of the fermentation mixtures was always 2.4 mg. of sample no. 1, or 1.2 mg. of sample no. 2, so that the mixtures contained about 24 times the quantity of active insulin required to produce rabbit convulsions under the above stated conditions. Before being added to the mixtures, these quantities of the samples (no. 2 being used in most cases) were dissolved in a little very dilute hydrochloric acid, and an equal volume of the same acid (called the "blank solution") was added to the control mixtures.

A fairly uniform distribution of the bacteria was secured by shaking the viscous milk culture with the skim-milk but even better checks in duplicate experiments were obtained by dropping the culture directly into the reaction bottles. Cultures were also made on a whey medium, which could be pipetted exactly, but the final accuracy obtained was no greater.

The fermentation was on the average allowed to continue for about 20 hours. The mixtures containing insulin began to coagulate about an hour sooner than the insulin-free controls. After the samples had coagulated so that the precipitates settled out quickly, the solutions were filtered; then 50 cc. portions were boiled for two minutes to expel carbon dioxide and at once titrated with 0.05 normal sodium hydroxide with the aid of phenolphthalein; from 6 to 7 cc. of this standard alkali being commonly required.

Several series of experiments made in this way showed that the mixtures containing insulin had produced, after the same interval of time, an amount of free acid greater than did the insulin-free mixtures, commonly by 20 to 25%, but occasionally by as little as 10% or by as much as 29%.

A set of experiments was made to determine directly the relative effects of the two insulin samples on the fermentation. The mixtures were so prepared as to contain the same quantity of rabbit-active insulin. Each sample increased the total acid by the same amount—namely, by about 20% more than in the mixtures which contained no insulin. This strongly

indicates that it is the insulin itself that accelerates the fermentation, and not the impurity associated with it, of which twice as much was present in one sample as in the other.

As a further control a set of experiments was made in which the effect of insulin inactivated by heating it on a boiling water-bath for 9 minutes with about 0.5 normal sodium hydroxide and then neutralizing the alkali, was compared with that of the same quantity of unheated insulin. It was found that, while the unheated insulin increased the yield of acid by 21%, the inactivated insulin gave the same result as the blank to which no insulin was added. In another set of experiments where the insulin was heated with only 0.01 normal sodium hydroxide to 100° for 15 minutes, the unheated insulin increased the acid yield by 26% and the heated insulin by 16%, over that in the blank experiment. This would indicate that the heated insulin was only partially inactivated; but it should be stated, that rabbit tests seemed to show that it had almost wholly lost its physiological activity—a result, however, that should be confirmed.

The preceding experiments were not carried out under completely sterile conditions, though precautions were taken to sterilize the flasks, water, glucose, and the skim-milk; and the insulin samples after precipitation from alcohol or ether had been immediately placed, and subsequently kept, in a vacuum desiccator. In order to make sure, however, that the effect on the fermentation was not due to bacteria introduced from the insulin sample, a solution of it was prepared and heated to 65° for 15 minutes. When plated both on nutrient agar and on lactose agar (with Andrade's indicator), it showed no growth in 48 hours; and when tested upon rabbits, it was found to have undergone little or no change in activity. Fermentation experiments made with this sterile insulin and under sterile manipulative conditions showed that it increased the yield of acid by 23%, or by about the same amount as in the preceding experiments.

A few other experiments may also be briefly mentioned. When a whey medium was substituted for the skim-milk, an increase of only 4% was observed, and the results were less concordant. When the concentration of the skim-milk and the quantity of culture were both reduced one-half, the increase in the amount of acid became negligible.

Insulin was found to increase the acid yield also when the fermentation was produced by Lactobacillus acidophilus; but in this case the increase was only about 8%.

The results of this investigation may be summed up in the statement that insulin has been proved to increase substantially (by 20–25 per cent) the quantity of acid produced by the fermentation of glucose under the influence of the organism Lactobacillus bulgaricus, and to a less extent under that of Lactobacillus acidophilus. Whether this effect is due to

stimulation of the growth of the organism, to increase in the decomposition of the glucose through co-enzyme action, or to some other cause, has not been determined. From the viewpoint also of developing a method of assaying insulin, the research is to be regarded as only a preliminary one; and it is to be continued in this direction, so as to find the best conditions for producing the maximum effect and for yielding concordant results in duplicate experiments, and to determine how the magnitude of the effect varies with the concentration of the insulin.

A NEW GROUP OF DYES FROM POISON GASES THROUGH THE 2-AMINOTHIAZOLES AS INTERMEDIATES. THE PREPARATION OF THIAZOLE DYES OF DOEBNER VIOLET TYPE[1]

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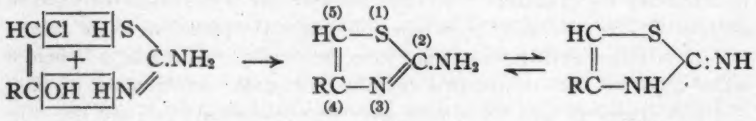
Communicated, August 28, 1924

Halogenated aldehydes and ketones of the type $RCO.CH_2X \rightleftharpoons RC(OH):CHX$ (X = halogen) include some of the most powerful lachrymatory compounds known, such as the halogenated acetones and chloroacetophenone used during the war as "tear gases."

Many years ago it was discovered[2,3] that 2-aminothiazoles are obtained easily from such compounds by condensation with thioureas:



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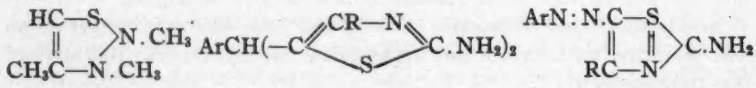
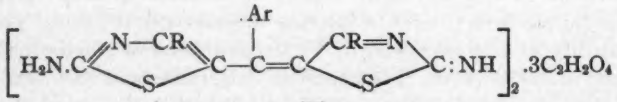


(III) (IV) (VI)



(V)

Ar = simple or substituted aromatic radical.
R = H, alkyl or aryl group.

Hantzsch and Weber,[4] and others[2,3,5,6,7,8,9,10] subsequently, studied various 2-aminothiazoles and came to the conclusion that such compounds existed in the two tautomeric forms represented by Formulas I and II.

Traumann[11] prepared the trimethyl derivative (III), and made the following statement concerning it:—"A Thiazole Green, corresponding to Malachite Green or Thiophene Green, could not be obtained from this dimethyl base, which is not to be wondered at in view of the disappearance of the supposititious analogy of this base to dimethylaniline. In general, trithiazylmethane dyes appear not to exist, probably because the *para* position is lacking in the azoles. Thus, the joint oxidation of thiazylamines with methylthiazylamine by the action of mercuric chloride, etc., likewise yields no trace of dye."

This pronouncement does not agree altogether either with our own views regarding the dye possibilities of these aminothiazoles or with our experimental results; for it has been observed frequently that sulfur in cyclic union is the equivalent of the —CH: CH— group, as is well illustrated in the close parallelism in physical and chemical properties between the benzene and thiophene series, or between the thiazoles themselves and the corresponding pyridines. The 2-aminothiazoles, therefore, carry the amino group in a position which is to all intents and purposes *para* to Position 5.

In support of this assumption, we have succeeded in condensing these 2-aminothiazoles with aromatic aldehydes, in the presence of hydrochloric acid, to monoaryldithiazylmethanes (IV), from which the corresponding carbinols and dyes, (V) have been obtained. Such condensations were accomplished with 2-aminothiazoles carrying alkyls instead of aryls in Position 4, thus demonstrating the fact that this condensation with aromatic aldehydes was not dependent upon an aryl group in that position, that such group did not participate in the reaction, and that therefore the attachment of the aldehyde residue was at Position 5.

The leucobases so obtained were generally colorless or pale yellow, the carbinols red-black, and the dyes (oxalates) green-black.

A comparison of certain properties of these new products with those triphenylmethane derivatives of analogous structure, discloses an interesting resemblance. The leucobases in both cases form crystalline addition products with benzene. Both groups of dyes form dark green crystals, those of the thiazole type being smaller, darker and of less marked coppery luster. The Malachite Green dyes are easily soluble in water, the thiazoles less readily; addition of excess of ammonium hydroxide solution precipitates the carbinol in both instances as a dark solid. Both dye silk, wool or mordanted (tannined) cotton, a green, the thiazoles giving

a bluer and duller shade and being tinctorially weaker. Both are fugitive in direct sunlight, and both give red solutions in excess of strong hydrochloric acid.

Although of Doebner Violet type, in the sense that the thiazole amino groups are unalkylated, these compounds give green dyeings, a bathochromic effect which doubtless is to be ascribed to the sulfur present in the molecule. Just as there is not any very striking difference between the shade produced by Doebner Violet itself and that produced by its derivative carrying a dimethylamino group in the *para* position on the free phenyl group, so here the shade is not greatly altered by using *p*-dimethylaminobenzaldehyde, in place of benzaldehyde, as the condensing agent.

As mentioned, the dyes prepared so far are inferior to Malachite Green, but the work is being continued with especial reference to the connection between structure and tinctorial properties, and in the hope that some useful products may be discovered.

The war "gases" used as initial materials were dichloro ether (for chloroacetaldehyde), chloroacetone and chloroacetophenone; the thiazoles were the 4-methyl- and 4-phenyl-2-aminothiazoles; and the aromatic aldehydes with which they were condensed were benzaldehyde, its *p*-chloro, *o*-, *m*- and *p*-nitro, *p*-dimethylamino, *o*- and *p*-hydroxy derivatives, and piperonal.

Further, we have learned that the aminothiazoles may be used as couplers for diazotized amines, and a number of new red azo dyes (VI) have been prepared in this way.

[1] The chloroacetophenone necessary for this investigation was presented by the Chemical Warfare Service, United States Army, through the courtesy of Brig.-Gen. Amos A. Fries, Chief, to whom our grateful acknowledgments are due.—M. T. B. and M. C.

[2] Traumann, *Ann.*, **249**, 35 (1888).

[3] Popp, *Ibid.*, **250**, 273 (1889).

[4] Hantzsch and Weber, *Ber.*, **20**, 3121 (1887).

[5] Wohmann, *Ann.*, **259**, 277 (1890).

[6] Schatzmann, *Ibid.*, **261**, 8 (1891).

[7] Naef, *Ibid.*, **265**, 109 (1891).

[8] Hantzsch and Schwab, *Ber.*, **34**, 834 (1901).

[9] Young and Crookes, *J. Chem. Soc.*, **89**, 59 (1906).

[10] Morgan and Morrow, *Ibid.*, **107**, 1291 (1915).

[11] Traumann, *Ann.*, **249**, 50 (1888).

THE SYNTHESIS OF TEREPHTHAL GREEN AND TEREPHTHAL BRILLIANT GREEN FROM CYMENE[1]

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Read before the Academy, April 29, 1924

Introductory.—In 1876, Otto Fischer[2] heated a mixture of *o*-phthalyl chloride and dimethylaniline at 100° and formed a compound to which he assigned Formula I. In the presence of zinc dust, at the same temperature, he obtained later[3] a "Phthalgruen," whose structure he represented by Formula II, dimethylanilinephthalein (V) being formed simultaneously. Subsequently, this Phthal Green was investigated by Haller and Guyot,[4] who established its constitution as a derivative of 9-phenylanthrone (IV) rather than of the structure shown by Formula III. More recently, Weitz[5] has prepared an *o*-Phthaldehyde Green, and Craver[6] has patented Malachite Green types produced from *o*-xylylaldehyde.

In our search of the literature, we failed to find any record of dyes of this class in the *meta*- or *para*-phthalic series, and hence undertook the preparation of such compounds as early as 1917.

In that year, Dr. C. P. Harris,[7] working under the direction of the senior author, conducted some preliminary experiments on the condensation of terephthalyl chloride with dialkylanilines, the object of which was to produce and investigate the terephthalic analogs of the Malachite Green dyes. Green dyes were actually obtained in these preliminary trials, but their investigation was suspended owing to the withdrawal of Dr. Harris to accept an industrial appointment. The present paper is therefore a continuation of the research inaugurated by Bogert and Harris.

The raw material for the synthetic work was the usual one where terephthalic acid is concerned, namely the "spruce turpentine condensate" from the paper mills, a readily available and economical source of cymene.

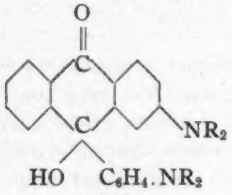
This hydrocarbon was oxidized to terephthalic acid,[8] the crude acid purified by crystallization of its methyl ester, the pure acid converted into terephthalyl chloride, and the latter condensed with dialkylanilines. The course of the reaction between the acid chloride and the dialkylaniline was determined by the presence or absence of such condensing agents as zinc chloride.

When the terephthalyl chloride and dimethylaniline were heated together at 198–215°, methyl chloride was evolved and the alkylanilide (VI) formed, a reaction similar to that noted by Hess[9] with benzoyl chloride and dimethylaniline, and by Staedel[10] in the case of acetyl bromide and dimethylaniline.

In the presence of zinc chloride, however, terephthalyl chloride and

dimethylaniline condensed smoothly, even at 100°, to a deep green dye of Malachite Green type (VII). By using diethyl- instead of dimethylaniline, the analogous Brilliant Green type was secured.

$R_2N.C_6H_4.CO.C_6H_4.CO.C_6H_4.NR_2HCl$ (I)



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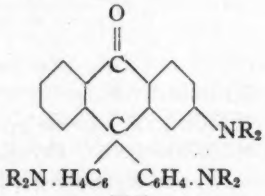

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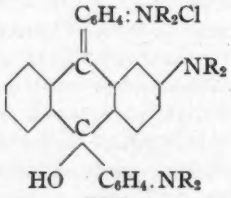

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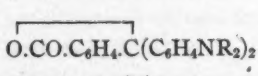

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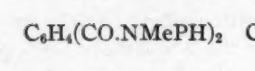
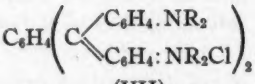
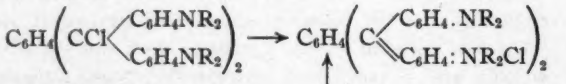


(VI)

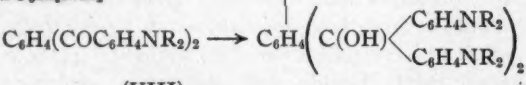


(VII)

(A) $C_6H_4(COCl)_2 + 2C_6H_4NR_2 \longrightarrow$



(B) $C_6H_4(COCl)_2 + 2C_6H_4NR_2 \longrightarrow$



(VIII)

The course of the condensation by which the dye is formed is represented by Series A above, rather than by Series B; for the former assumes that the first step consists in the loss of water, whereas the latter predicates a preliminary removal of hydrogen chloride. Experiments have shown that the dye is formed, not only when zinc chloride is used as the condensing agent, but also when the latter is replaced by phosphorous pentoxide, oxychloride or pentachloride, which are primarily dehydrating agents and not hydrogen chloride eliminants. Further, if the condensation de-

pended upon initial removal of hydrogen chloride, the product should be a colorless diketone (VIII), of Michler ketone type, and not a dye. The presence of hydrochloric acid, or of a phosphorous halide, would be requisite to condense this diketone with a dialkylaniline to a dye.

In tinctorial properties, these new dyes compare favorably with Malachite and Brilliant Green. On wool (1.5% dyeings), the shade is distinctly yellower than the older dyes; in direct sunlight, they are slightly more fugitive; but appear to be superior in fastness to washing, milling, stoving and perspiration tests. Dyeings with Terephthal Brilliant Green are lighter in shade than those made with Terephthal Green, just as Brilliant Green itself gives lighter shades than Malachite Green under similar conditions.

Experimental Part.—"Spruce turpentine condensate," from the paper mills, was washed with caustic alkali and distilled with steam. The crude cymene so obtained was sufficiently pure for our purposes. It was oxidized by sodium dichromate and sulfuric acid, as recommended by Bogert and Harris.[8] By the use of a large excess of the dichromate (440 g. per 25 g. of cymene), the yield of crude terephthalic acid was increased to 85% of the cymene consumed in the operation. This crude acid contained about 7–8% of *p*-toluic acid and small amounts of chromium salts. It was converted into its methyl ester, using either hydrogen chloride or concd. sulfuric acid as condensing agent, which was crystallized from alcohol; yield, 70%. From the mother-liquors, the *p*-toluic acid was recovered by evaporation of the alcohol, hydrolysis of the ester by boiling it with 10% sodium hydroxide solution, then acidifying and distilling with steam. The *p*-toluic acid thus driven over was crystallized from alcohol and melted at 180° (corr.); yield, 7.1% the weight of crude terephthalic acid employed. Pure terephthalic acid was obtained by hydrolysis (by 10% sodium hydroxide solution) of its methyl ester; yield, 95%, calculated to the ester.

Terephthalyl Chloride was produced from the acid (20 g.), phosphorous oxychloride (56 g.) and pentachloride (90 g.), by the method of Locher;[11] b. p., 263–266°, m. p. 82° (corr.); yield, 90%.

Terephthalmethylanilide (VI).—A mixture of terephthalyl chloride (5 g.) and dimethylaniline (12 g.) was heated for 6 hours at 100°, but no condensation occurred.

When a similar mixture was boiled for 3 hours over a naked flame, the temperature rose gradually from 198° to 215°, at which latter point it remained constant. After continuing the boiling for an hour longer, the mass was dissolved in concd. hydrochloric acid, the solution filtered and the filtrate diluted with 5 volumes of water. The greenish precipitate was collected, boiled for 2 hours with 10% sodium hydroxide solution, removed, washed and dried. It then appeared as a yellow solid; yield,

78%. Crystallized repeatedly from toluene, it formed beautiful pale yellow flat prisms, m. p. 212–213° (corr.); yield, 28%.

Anal. Calc. for $C_{22}H_{20}O_2N_2$: C, 76.74; H, 5.81; N, 8.14. Found: C, 76.87, 76.77; H, 5.87, 5.82; H, 8.20.

The alkaline filtrate from this product yielded 0.5 g. of terephthalic acid when acidified.

The analytical figures obtained for the product melting at 212–213° (corr.) agree with those calculated for the methylanilide. The reaction was repeated, therefore, using 20 g. of the acid chloride and 48 g. of the dimethylaniline. The effluent gases were past into dry thiophene-free benzene containing some anhydrous aluminum chloride. At the close of the reaction, toluene was detected in the benzene, thus proving the presence of methyl chloride in these effluent gases

The methylanilide was unchanged when boiled for 7 hours with an excess of acetic anhydride, or when dissolved in alcohol and treated with hydrochloric acid and sodium nitrite at 0°. Boiling concd. hydrochloric acid hydrolyzed it to terephthalic acid and methylaniline, of which the former was identified by conversion into its methyl ester, and the latter by formation of methylacetanilide (m. p. 102°, corr.).

A further proof of the identity of this methylanilide was supplied by its synthesis from terephthalyl chloride and monomethylaniline, in boiling toluene solution. The product isolated was the same in appearance and melting-point as that obtained from dimethylaniline, and a mixture of the two products melted sharply at the same point (212–213°, corr.).

Terephthal Green (VII).—A solution of 5 g. of terephthalyl chloride in 12 g. of dimethylaniline was heated to 100° and 7 g. of finely ground zinc chloride stirred in. After 3 hours' heating, the mixture had congealed to a hard dark green solid. This was dissolved in 200 cc. of warm water and the excess of dimethylaniline removed by distillation with steam. After adding a few drops of acid, to dissolve any basic zinc chloride, the solution was filtered, the filtrate evaporated to about 50 cc. and the dye precipitated by the addition of saturated sodium chloride solution. It was purified by resolution in the minimum quantity of water and reprecipitation by salt, and was finally washed with small amounts of water and dried in a vacuum desiccator. The double zinc chloride thus obtained was a green-black solid, of coppery luster; yield, 50%.

Anal. Calc. for $C_{40}H_{44}N_4Cl_2.3ZnCl_2$: Zn, 18.47; Cl, 26.79. Found: Zn, 18.09, 18.25; Cl, 27.12.

The proportion of dye to zinc chloride in this and in the succeeding dye differs somewhat from that in the Malachite Green double salt, where the molar ratio of dye to zinc chloride is 3: 2.

Terephthal Brilliant Green, prepared similarly, formed a double zinc chloride as a black-green solid, of bronze luster; yield, 48%.

Anal. Calc. for $C_{48}H_{60}N_4Cl_2.3ZnCl_2$: Zn, 16.72; Cl, 24.23. Found: Zn, 16.37, 16.42; Cl, 24.62.

Comparison of the Dyes.—The following tests were carried out, under as nearly as possible identical conditions, with Malachite Green, Brilliant Green, and the two terephthalic analogs just described. All dyed silk and wool direct, with apparently equal facility, but were not substantive for cotton.

Wool was dyed with a 0.1% solution of the dye containing an amount of dye equal to 1.5% the weight of the fabric used and 20 g. of sodium chloride per 150 cc. of solution. The dyeing was continued at the boiling-point of the solution until the bath was practically exhausted.

1. *Shade.*—In tinctorial strength, the two classes of dyes seemed about equal. The terephthalic derivatives dyed a yellower green than the corresponding triphenylmethane derivatives, the ethyl derivatives in both cases yielding lighter shades than the methyl.

2. *Fastness to Light.*—The newer dyes proved even more fugitive than the older ones.

3. *Washing Test.*—Dyed samples of cloth were wrapped in pieces of undyed cloth and worked for 5 mins. in a solution containing 5 g. of soap per liter of water, then soaked in the same solution for 15 mins. at 40°, rinsed in fresh water and dried. All four dyes lost a little color by this treatment. The older dyes bled into the undyed cloth, but no such bleeding occurred with the newer ones.

4. *Milling Test.*—Dyed samples wrapped in undyed cloth were stirred and kneaded for 10 mins. at 60° in a solution containing 5 g. of soap and 4 g. of sodium carbonate per liter. Bleeding was much less with the terephthalic dyes than with the triphenylmethane derivatives. Both lost color slightly in the treatment.

5. *Fastness to Alkali.*—Dyed samples were moistened with dilute and with concd. caustic alkali, dried and brushed off. All four were unchanged by the dilute alkali and turned yellow by the concd.

6. *Fastness to Acid.*—All four samples were unchanged when boiled for 10 mins. with 10% hydrochloric acid.

7. *Perspiration Test.*—Dyed samples were wrapt in pieces of undyed cloth, then soaked in a solution containing 100 g. of sodium chloride and 100 g. of acetic acid per liter, removed and heated at 40° for 24 hours. Bleeding occurred with the older dyes, but not with the terephthalic derivatives.

8. *Stoving.*—Suspended for 12 hours in an atmosphere of sulfur dioxide, the triphenylmethane dyes faded more rapidly than did the terephthalic derivatives; although both were nearly colorless at the end of the exposure.

9. *Bleaching.*—Dyed samples were soaked for 15 mins. in a solution containing 38 g. of sodium hypochlorite in 2 liters of water. All four samples lost color, but regained it upon exposure to the air.

Summary.—*1.* New dyes, of Malachite Green type, have been synthesized from terephthalyl chloride (from cymene) and dialkylanilines, in the presence of zinc chloride, which dye wool or silk a yellower green than that produced by Malachite or Brilliant Green. In general, these newer dyes compare favorably with the older triphenylmethane derivatives in tinctorial power, fastness, etc.

2. Terephthalyl chloride and dimethylaniline, in the absence of zinc chloride, react at higher temperatures (198–215°) with evolution of methyl chloride and formation of terephthalmethylanilide.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 456]

[1] The cymene for this investigation was supplied by the Hollingsworth and Whitney Company, Winslow, Maine. We welcome this opportunity to express our appreciation of their courtesy.—M. T. B. and P. S. N.

[2] Otto Fischer, *Ber.*, **9**, 1753 (1876).

[3] Otto Fischer, *Ann.*, **206**, 107 (1881).

[4] Haller and Guyot, *Compt. rend.*, **125**, 221, 1153 (1897).

[5] Weitz, *Ann.*, **418**, 1 (1919).

[6] Craver, U. S. Pat. No. 1,470,554 (Oct. 9, 1923); *Color Trade J.*, **14**, 12 (1924).

[7] C. P. Harris, *Dissertation*, Columbia Univ., 1917, p. 42.

[8] Bogert and Harris, *J. Am. Chem. Soc.*, **41**, 1680 (1919).

[9] Hess, *Ber.*, **18**, 685 (1885).

[10] Staedel, *Ibid.*, **19**, 1947 (1886).

[11] Locher, *Bull. soc. chim.*, (3) **11**, 927 (1894).

FURTHER EXPERIMENTS IN THE FIELD OF THE TEREPHTHALIC ACID DERIVATIVES[1,2]

BY MARSTON TAYLOR BOGERT AND PHILIP SAMUEL NISSON

CHEMICAL LABORATORIES, COLUMBIA UNIVERSITY

Read before the Academy, April 29, 1924

INTRODUCTORY

Some years ago, Bogert and Harris[3] described the synthesis of *para*-di (hydroxyisopropyl) benzene from methyl terephthalate and methyl magnesium iodide. Its structure suggested the possibility of its possessing hypnotic or local anesthetic properties and, through the coöperation of our good friends, Drs. Arthur W. Dox and Oliver Kamm, of Parke, Davis & Co., and Prof. Arthur D. Hirschfelder, of the University of Minnesota, pharmacodynamic experiments later were carried out. The results of the tests are recorded in the experimental part of this paper.

The lack of physiological activity so disclosed seemed referable, in part at least, to physical and chemical defects which we believed might be

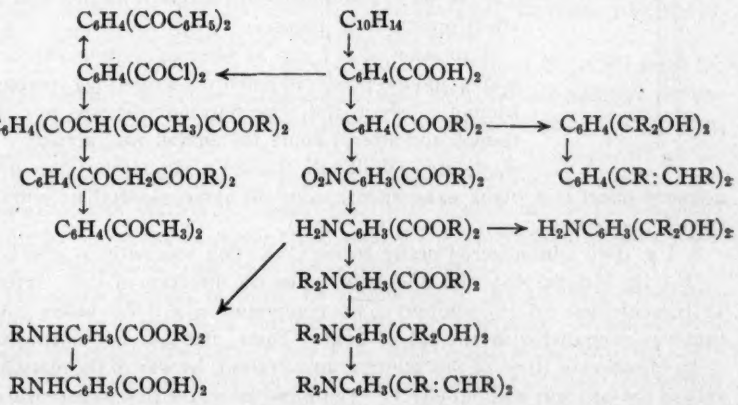
remediable. The outlook appeared sufficiently promising to justify further experiments, and their results are submitted herewith.

The first line of attack was the attempted preparation of higher homologous pinacones, in the hope of thereby obtaining compounds of greater physiological activity. The attack failed because of the instability of the pinacones so formed, all of which lost water readily and rapidly with production of di-olefins. With the exception of the tetrethyl compound, these di-olefins polymerized so easily that neither they nor their progenitor pinacones could be isolated in a condition of even approximate purity.

Another method of synthesizing these pinacones, which consisted in the application of the Grignard reaction to *para*-diketones of the type $C_6H_4(CO.R)_2$ was begun, but the experiments have not advanced much beyond the preparation of some of the requisite diketones. Incidentally, it was found that aryl magnesium halides condensed with terephthalyl chloride to such diketones far more satisfactorily than the alkyl magnesium halides.

A third series of experiments was concerned with the preparation of analogous aminated pinacones, but it too encountered similar obstacles due to the instability of these pinacones and, although a number of new compounds were synthesized and studied, the goal originally sought was not attained.

The major lines of the investigation may be exhibited thus:

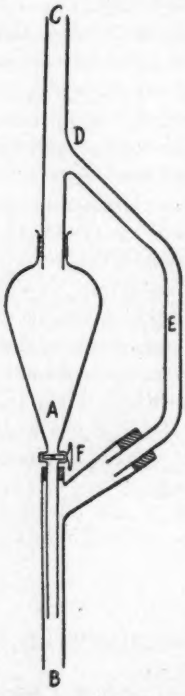


EXPERIMENTAL PART

Tetramethyl para-Xylylene Glycol (para-di (Hydroxyisopropyl)benzene), $C_6H_4(C(CH_3)_2OH)_2$, was prepared by a modification of the method of Bogert and Harris,[3] using the apparatus shown in the accompanying figure, which was made up from a separating funnel, an addition tube and a large T tube.

The Grignard reagent was prepared in the customary manner in a round-

bottom flask, which was then attached at B. A plug of glass wool was placed in the bottom of the separatory (A), to prevent clogging of the outlet, and upon this glass wool the methyl terephthalate rested. Connection with the reflux condenser was established at C.



In carrying out a Grignard reaction in this apparatus, A should be kept about half full of ether. In case the ether distils up through the side arm (E) faster than it runs down through the stopcock (F), it will collect in A until it reaches D, after which it will simply reflux through E. Hence, the apparatus does not demand close and constant attention, and the rate of flow through F can be adjusted to meet the needs of the reaction. We believe that it will be found convenient in other cases also, where difficultly soluble compounds are to be subjected to the action of Grignard reagents.

Pharmacodynamic Examination of Tetramethyl para-Xylylene Glycol (paradi(Hydroxyisopropyl)benzene).—(*A.*) By Dr. Oliver Kamm.—A solution of 3 mg. in 1 cc. of water, administered intraperitoneally, had no effect upon a 20 g. mouse.

A solution of 6–7 mg. in olive oil, administered to a 20 g. mouse, produced a distinct stupefying (perhaps hypnotic) effect, but complete narcosis was not obtained, and after 3 hours the animal was normal. A duplicate experiment showed a similar but less pronounced effect. A blank experiment, using oil alone, showed no similar stupefying action.

A 1 g. dose administered orally to an 11 K. dog was without effect.

(*B.*) By Messrs. Kole and Wickham, under the direction of Prof. Arthur D. Hirschfelder.—A 1% solution of the compound in a 0.9% saline solution was prepared with the aid of heat. Taste, flat and not astringent.

An injection of 10 cc. of this solution into a rabbit, by way of the marginal vein of the ear, was without effect. Ten mins. later, the dose was repeated likewise without apparent result. Pupils, respiration and heart beat remained normal and there was no loss of locomotion, muscle tone, renal or rectal sphinctus, and no urination. The animal was under observation for 3 hours and exhibited no visible effects.

Five cc. of the solution was injected hypodermically into the ear. No sloughing occurred and the ear returned to normal.

A frog was single-pithed and a cotton compact of the solution was applied to the surface of one limb. The sensory stimulus was supplied by a

0.4% acetic acid, and also by dilute hydrochloric acid, but at all times the limb was flext upon application of the acid. Crystals of the compound were then added to the saturated compact without result.

Another frog was taken and 5 cc. of the 1% solution was injected into the dorsal lymph sac, but no ill effect was observed.

Different dilutions of the compound were applied without effect to the exposed nerve of a frog. Then a piece of cotton, dampened with the 1% solution and covered with crystals of the compound, was applied for 10 mins. directly to the nerve, but no effect was noted.

The compound therefore does not function as a local anesthetic, and is too difficultly soluble. It causes no irritation or sloughing.

3-para-Phenylene-bis(2-pentene), $C_6H_4(C(C_2H_5):CHCH_3)_2$.—Ethyl magnesium iodide (50% excess) and methyl terephthalate were condensed in the apparatus described above. The reaction was complete in 3–4 hours. The addition compound was hydrolyzed by ice and hydrochloric acid, the ether layer separated, the ether removed, and the residue digested for 2 hours with a 10% sodium hydroxide solution at 100°, to remove unaltered ester. The cooled mixture was extracted with ether, the ether extract washed with water, dried over calcium chloride, the ether driven off and the residue distilled under reduced pressure. A pale yellow liquid was obtained, b. p. 149–151° (20 mm.), of pleasant and persistent pinene-like odor; yield, 46%, allowing for the recovered ester.

Anal. Calc. for $C_{16}H_{22}$: C, 89.64; H,10.36. Found: C, 88.96; H,10.15.

The product therefore is the unsaturated hydrocarbon and not the expected pinacone. It decolorized instantly a carbon tetrachloride solution of bromine.

Attempted Preparation of Tetra-n-butyl para-Xylylene Glycol.—The condensation was carried out using 12.5 g. of magnesium, 70 g. of *n*-butyl bromide, 500 cc. of absolute ether and 16.7 g. of methyl terephthalate. This provided a 50% excess of the Grignard reagent.

The crude product obtained by hydrolysis of the addition compound proved to be a heavy oil which could not be congealed. When distilled under diminished pressure, it lost water and yielded a fraction, b. p. 230–232° (19 mm.), which was probably the 5-*para*-phenylene-*bis*(4-nonene), $C_6H_4(C(C_4H_9):CHC_3H_7)_2$, since it immediately decolorized a carbon tetrachloride solution of bromine; yield, equal to about 25% the weight of initial ester used.

Attempts further to rectify this fraction by distillation at low pressures, changed most of it into tar, and no pure product was isolated.

para-Diacetylbenzene, $C_6H_4(COCH_3)_2$.—Terephthalyl-*bis*(ethyl acetoacetate), $C_6H_4(COCH(COCH_3)COOR)_2$, was prepared by the method of Berend and Herms[4] from terephthalyl chloride and the sodio derivative of ethylacetoacetate below 10°; m. p. 102.5°(corr.); yield, 60%.

This was hydrolyzed by the action of ammonium hydroxide and chloride, following the process of Perkin and Weizmann,[5] to terephthalyl-*bis*(ethyl acetate), $C_6H_4(COCH_2COOR)_2$; m. p. 70°(corr.); yield, 60%.

As already recorded by Berend and Herms,[4] this latter ester yields the *para*-diacetylbenzene when boiled with 10% sulfuric acid; m. p. 113° (corr.); yield, 85% or, calculated back to the initial terephthalyl chloride, 30.6%. The compound was synthesized first, however, by Ingle,[6] through an analogous series of reactions, using ethyl malonate instead of ethyl acetoacetate.

Attempts to obtain ketones of this type by the action of alkyl magnesium halides upon terephthalyl chloride were unsuccessful, but when aryl halides were substituted for the alkyl derivatives the results were more satisfactory.

para-Dibenzoylbenzene.—A Grignard reagent prepared from 1.2 g. of magnesium, 7.7 g. of bromobenzene and 125 cc. of absolute ether, was added drop by drop to a mechanically stirred solution of 5 g. of terephthalyl chloride in 65 cc. of absolute benzene, and the mixture left overnight at the laboratory temperature. It was then hydrolyzed by dilute (1:1) hydrochloric acid, the solvents removed and the residue digested for an hour with a 10% caustic soda solution at 80°. The insoluble diketone was collected, washed, dried and crystallized from benzene, when it formed colorless plates, m. p. 160–161° (corr.), similar in appearance and melting-point to the *para*-dibenzoylbenzene obtained by Noelting and Kohn[7] by the Friedel-Crafts reaction.

A few experiments were carried out also with *para*-dibromobenzene and magnesium, in dry ether solution; but hydrolysis of the product gave in every instance monobromobenzene, showing that only one of the bromine atoms reacted with the magnesium, a result which is in accord with the experience of Yo..ich[8] and of Pink.[9]

Methyl Nitroterephthalate, $O_2NC_6H_3(COOR)_2$, was obtained by the direct nitration of methyl terephthalate, as described by Kauffmann and Weissel.[10] By careful cooling during the nitration we succeeded in raising the yield to 90° (m. p., 96°, corr.).

Methyl Aminoterephthalate, prepared by reduction of the nitro ester with stannous chloride and hydrochloric acid, following the method of the same investigators, formed pale yellowish crystals, m. p. 133° (corr.); yield, 75%.

Some trouble was encountered in handling the tin salts until the correct concentration of hydrochloric acid was determined. If the concentration of acid is too low, these salts are apt to interfere with the crystallization of the ester; whereas, if correct, they all dissolve when the solution is boiled.

Methyl Dimethylaminoterephthalate.—Here too we followed the lead of Kauffmann and Weissel, and prepared this compound by the action of methyl sulfate upon the methyl aminoterephthalate, separating the mono-

methyl derivative by precipitating it as the nitroso derivative; yield 67% (m. p., 70.5°, corr.).

An attempt to raise the yield by continuing the initial heating beyond the stated 5 hr. period failed to accomplish the desired result, although it reduced the amount of monomethyl derivative formed.

Methyl Ethylaminoterephthalate, $C_2H_5NHC_6H_3(COOCH_3)_2$.—A mixture of 5 g. of methyl aminoterephthalate and 10 g. of ethyl iodide (33% excess) was heated in a sealed bomb tube for 2 hours at 100°. The tube contents was evaporated to dryness, the residue dissolved in dilute (15%) hydrochloric acid and the ester precipitated by addition of alkali. Crystallized from 70% alcohol, it formed lustrous greenish yellow flat needles, m. p. 83.5° (corr.); yield, 35%.

Anal. Calc. for $C_{12}H_{15}O_4N$: C, 60.73; H, 6.38; N, 5.95. Found: C, 60.82; H, 6.34; N, 5.97.

The alkaline mother-liquor from the ester was acidified and *ethylaminoterephthalic acid* precipitated; yield, 60%. This was esterified by the action of methyl alcohol and concd. sulfuric acid, and the ester purified by crystallization from 70% alcohol. It proved to be identical in all respects with the ester (m. p., 83.5°, corr.) described above. With hydrochloric acid and sodium nitrite, it formed a nitroso derivative.

Methyl Diethylaminoterephthalate, $(C_2H_5)_2NC_6H_3(COOCH_3)_2$.—A mixture of 10 g. of methyl aminoterephthalate and 30 g. of ethyl sulfate (about 50% excess) was heated for 4 hours at 150°, after which it was digested for a few hours at 100° with an excess of concd. sodium carbonate solution, to destroy any unaltered ethyl sulfate. The ethylated amino ester separated as an oil, which was collected with ether, the solvent evaporated, the residue dissolved in dilute (15%) hydrochloric acid and treated at 0° with a saturated aqueous solution of sodium nitrite. Only a slight turbidity resulted and this was removed by shaking with a little ether. The aqueous solution was made alkaline, the separated amino ester collected with ether, the ethereal solution dried with calcium chloride and distilled under reduced pressure. The product was a yellow heavy highly refracting oil, b. p. 191–192° (20 mm.); yield, 80%.

Anal. Calc. for $C_{14}H_{19}O_4N$: C, 63.36; H, 7.22; N. 5.28. Found: C, 63.69; H, 7.24; N, 5.42.

The Behavior of Aminoterephthalic Esters with Alkyl Magnesium Halides.—Methyl aminoterphthalate was subjected to the action of methyl magnesium iodide, ethyl magnesium iodide and *n*-butyl magnesium bromide, but only gummy products resulted and no pure pinacones were isolated.

2-(Dimethylamino - para - phenylene) - bis - (1 - propene), $(CH_3)_2NC_6H_3(C(CH_3):CH_2)_2$.—The Grignard reagent was prepared from 4.5 g. of magnesium, 26.3 g. of methyl iodide and 300 cc. of absolute ether. At the boiling-point of the solution, 10 g. of methyl dimethylaminoterephthalate dissolved

in 75 cc. of absolute benzene was added very slowly. After the addition of all ester, the solution was boiled for an hour longer and left overnight at laboratory temperature. It was then hydrolyzed by ice and dilute (1:1) hydrochloric acid, the ether and benzene were removed and the solution was made alkaline with ammonium hydroxide. The viscous precipitate was digested for 2 hours at 100° with dilute (10%) caustic soda solution, to remove unchanged ester, and was finally distilled repeatedly under diminished pressure. A fraction was separated, b. p. 190–192° (25 mm.), which congealed to a yellow solid. Crystallized from dilute alcohol, small yellowish crystals were obtained, m. p. 62–63° (corr.); yield, 35%.

Anal. Calc. for $C_{14}H_{19}N$: N, 6.96. Found: 7.01, 6.94

The substance decolorized immediately a carbon tetrachloride solution of bromine.

2-(Diethylamino-para-phenylene)-bis-(1-propene), prepared similarly from 4.5 g. of magnesium, 26.3 g. of methyl iodide and 11 g. of diethylaminoterephthalic ester, likewise gave a heavy oil, which may have been the crude pinacone, but from which no pure pinacone could be isolated. Distilled under reduced pressure, it yielded a fraction, b. p. 195–197° (18 mm.), as a yellow heavy oil, which was probably the di-olefin derivative.

Anal. Calc. for $C_{16}H_{23}N$: N, 6.11. Found, 6.25.

Amino Tetraphenyl-para-xylylene Glycol, $H_2NC_6H_3(C(C_6H_5)_2OH)_2$, was obtained from the aminoterephthalic ester and phenyl magnesium bromide, by much the same process as recorded in the case of the last mentioned compound (excepting the distillation), using 7.94 g. of magnesium and 68 g. of bromobenzene to 10 g. of the amino ester. The crude product was crystallized 13 times from toluene, using Norite for many of these crystallizations, and then formed minute pale yellowish prismatic crystals, which lost their crystalline form at 110° and melted at 202° (corr.); yield, only 7%.

Anal. Calc. for $C_{32}H_{27}O_2N$: C, 83.98; H, 5.95; N, 3.06. Found: C, 83.66; H, 5.84; N, 3.17.

Dimethylamino Tetraphenyl-para-xylylene Glycol, $(CH_3)_2NC_6H_3(C(C_6H_5)_2OH)_2$.—The synthesis of this compound was accomplished in similar manner from 2.3 g. of magnesium, 14.5 g. of bromobenzene and 5 g. of methyl dimethylaminoterephthalate. Purification of the crude product was effected by crystallization from benzene. The pure compound appeared in colorless microscopic short needles, m. p. 185° (corr.); yield, 45%.

Anal. Calc. for $C_{34}H_{31}O_2N$: N, 2.89. Found, 2.85, 2.96.

Diethylamino Tetraphenyl-para-xylylene Glycol, from 2.1 g. of magnesium, 13 g. of bromobenzene and 5 g. of methyl diethylaminoterephthalate, also was purified by crystallization from benzene, and formed a colorless pulverulent solid, m. p. 179° (corr.); yield, 49%.

Anal. Calc. for $C_{36}H_{35}O_2N$: N, 2.73. Found, 2.90, 2.80.

SUMMARY

1. Attempts to prepare pinacones of the type $C_6H_4(CR_2OH)_2$ by the action of Grignard reagents upon terephthalic or aminoterephthalic esters, failed in the case of the alkyl derivatives, but succeeded with the aryl magnesium halides.

2. The tetralkyl pinacone types lost water easily with formation of di-olefins which then generally polymerized to gums.

3. The tetramethyl pinacone has been investigated pharmacologically and found to possess little, if any, physiological activity. In the case of the other alkylated pinacones, only the di-olefin or gums were obtained.

4. The tetraryl pinacone types were too difficultly soluble to be of pharmacological interest.

5. Various new compounds have been synthesized and investigated, and some old ones have been prepared by new methods.

6. The apparatus of Bogert and Harris, for carrying out the Grignard reaction with difficultly soluble compounds, has been simplified.

[1] See these PROCEEDINGS.

[2] We are indebted to the Hollingsworth and Whitney Company, of Waterville, Maine, for the "spruce turpentine condensate" which served as the initial material for this investigation.—M. T. B. and P. S. N.

[3] Bogert and Harris, *J. Am. Chem. Soc.*, **41**, 1676 (1919).

[4] Berend and Herms, *J. prakt. Chem.*, [2], **74**, 123 (1906).

[5] Perkin and Weizmann, *J. Chem. Soc.*, **89**, 1655 (1906).

[6] Ingle, *Ber.*, **27**, 2526 (1894).

[7] Noelting and Kohn, *Ibid.*, **19**, 147 (1886).

[8] Yocich, *J. Russ. Phys.-Chem. Soc.*, **34**, 971 (1902); **36**, 8 (1904).

[9] Pink, *J. Chem. Soc.*, **123**, 3418 (1923).

[10] Kauffmann and Weissel, *Ann.*, **393**, 10 (1911).

A STATISTICAL DISCUSSION OF SETS OF PRECISE ASTRONOMICAL MEASUREMENTS, IV; THE MASS-RATIO IN BINARIES

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From lack of data, the assumption has often been made that the masses of the components of a binary system tend toward equality.[1] Although there is little good material for statistical discussion, its implications are important. We have fairly accurate total masses and mass-ratios for a dozen visual binaries and accurate mass-ratios for about 60 spectroscopic binaries. If we put $x = \log_{10}(m'/m)$ and take the mass-ratio both ways (m'/m and m/m') in each pair we obtain a necessarily symmetrical distri-

bution of x about its mean, 0. We found 69 systems that seem worthy of inclusion in the discussion and they give 138 values of x. The value of the standard deviation of x is $\sigma_x = 0.26 \pm .02$ and that of Pearson's constant β_2 (the ratio of the fourth moment about the mean to the square of the second moment about the mean) is $\beta_2 = 4.3 \pm 0.4$. The distribution therefore, is statistically speaking, not significantly different from the normal error curve ($\beta_2 = 3.0$).[2] In our previous note (these PROCEEDINGS, **10,** 394, 1924) we showed that for the sun and 14 nearby binaries the standard deviation of the logarithms of the masses from their mean was $\sigma = 0.36 \pm 0.03$. The value of σ for the logarithmic mass ratios of these 14 systems is 0.30 ± 04. It follows that the inclusion of the additional data from the spectroscopic pairs makes no significant change in the dispersion of x about its mean.

We saw before that the value of σ was almost the same (0.36) whether we treated the stars as individuals or as systems. Now if r be the coefficient of correlation between the logarithmic masses of the components in binaries we may write

$$\sigma_x^2 = 2\sigma^2 - 2r\sigma^2 \quad \text{or} \quad r = 1 - \sigma_x^2/2\sigma^2.$$

If we use $\sigma_x = 0.26$ and $\sigma = 0.36$ we find $r = 0.74$ and there appears to be a high degree of correlation between the masses in the pairs, or, otherwise expressed, a great tendency for the masses to be equal, which is in accord with the assumption generally made. It should not be overlooked, however, that there is probably a strong observational selection at work. Very dissimilar masses would mean statistically very different magnitudes and diminish the probability of detection and measurement of the binary. Another way to put the matter is to ask: What would be the standard deviation of the logarithmic mass-ratio of the 406 hypothetical binaries that could be constructed by pairing in all possible ways the 29 stars of our previous note with $\sigma = 0.36$? The result would be $\sigma_x' = 0.50$ which is much larger than the value 0.26 found above. But in our present list of 69 binaries there is none with a mass ratio greater than 5; whereas in the 406 hypothetical binaries there are 79. Now if it be assumed that these high mass-ratios if existent would not be observed and measured, we find that the value of σ for the remaining 327 pairs would be only 0.31 which is a great reduction from 0.50 and is not far from the value 0.26 actually found.

To discuss the observational selection we may proceed as follows: Let the total number of binaries be N and the number of those discovered and measured $N'(= 69)$. If the ratio of the masses were in the manner that would arise from random mating of stars with $\sigma = 0.36$, the frequency distribution would be

$$f(x) = \frac{2N}{0.50\sqrt{2\pi}} e^{-x^2/2(0.50)^2} = \frac{2Ne^{-2x^2}}{0.5\sqrt{2\pi}}.$$

The frequency distribution calculated for the 69 measured binaries is

$$\varphi(x) = \frac{2N'}{0.26\sqrt{2\pi}}\, e^{-x^2/2(0.26)^2} = \frac{2N'\, e^{-7.4x^2}}{0.26\sqrt{2\pi}}.$$

The average chance of finding a binary in our set would be N'/N; but the chance of finding one of specified logarithmic mass ratio x would be

$$\varphi(x)/f(x) = 1.9\, e^{-5.4x^2}\, .N'/N,$$

and there would thus be about double the average chance (N'/N) for finding on our list a binary with equal masses.

Let it be assumed that the relation between the logarithm of the mass and the luminosity M is linear and for definiteness that $x_1 - x_2 = -0.07$ $(M_1 - M_2)$, which is close to the value obtained by several investigators. Then the following table is readily computed.

MASS RATIO	DISCOVERY CHANCE*	LUMINOSITY RATIO
20 : 1	1 : 9000	10^8: 1
10 : 1	1 : 220	4×10^6: 1
5 : 1	1 : 14	25000 : 1
3 : 1	1 : 3.7	600 : 1
2 : 1	1 : 1.6	70 : 1
1.5 : 1	1 : 1.2	11 : 1
1 : 1	1 : 1	1 : 1

* Here the chance of discovery is estimated relative to the chance of discovering stars of equal mass, i.e., it is ϕ/f divided by $1.9N'/N$.

In view of the very great luminosity ratios it might appear reasonable to believe that the discovery chances have been over-estimated and that, when the discovery chance is considered, the observed mass-ratios are more scattered than would be the case if the two components were selected at random. And this confirms our remark in the previous note that whenever the masses of enough additional binaries shall have been measured to re-establish the statistical homogeneity, it will not unlikely be found that the dispersion of logarithmic masses is greater than 0.36.

Thus the general conclusion from the meager data of reasonable precision that we possess is that there is a considerable probability that the apparent clustering of the mass-ratios about unity is due to observational selection and that the actual association may be not materially different from random mating.

[1] Cf. Eddington, *Stellar Movements*, p. 23, and Boss, *Preliminary General Catalogue*, p. xxiii.

[2] The series of 138 is too small to make a departure of three times the probable error significant; the numerical constants of the distribution would be altered somewhat by discarding one binary for which the mass ratio is nearly double (or half) that of the next highest (smallest).

NOTE ON THE THERMOKINETICS OF DOLICHODERINE ANTS

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In an earlier communication I reported on the relation of speed to temperature for ants of the species *Liometopum apiculatum* Mayr. The observations were made on Mount Wilson, California, where this and closely related species are conspicuous features of the ant fauna.[1] The observations showed that meteorological conditions other than temperature had little effect on the field activities of the *Liometopa*. But the change in the speed along the patrolling files with the changing temperature was very marked. As the temperature increases 30° C, the speed increases fifteen fold. Observation of the time required to run a distance of thirty centimeters, taking an average for ten or twenty individuals, suffices to indicate the air temperature within one degree. The optimum temperature was not reached for this genus, under natural field conditions, since for temperatures above 38.5° the ants in the colonies under observation no longer attempted to run the patrols. By analyzing the results it was found that the values of Q_{10} decrease from about four to less than two.

Observations of temperature and speed have since been made on *L. occidentale*, *L. luctuosum* (or a similar undescribed species), *Dorymyrmex pyramicus* subsp. *brunneus*, *Iridomyrmex analis*, *I. humilis*, and *Tapinoma sessile*. All these forms belong to the subfamily Dolichoderinæ. They are suitable for the quantitative measurement of speed because they run day and night and generally have large colonies, and especially because of their almost universal trail-running habits.

The reactions of all Dolichoderines investigated are qualitatively much the same as reported previously for *L. apiculatum*, but only for *T. sessile* and the Argentine ant, *I. humilis*, were the observations sufficiently systematic to merit numerical presentation. In tables I and II the work on the two species is given in summarized form. The observations are recorded in Pacific Standard Time, the temperatures are on the centigrade scale, the speed is in centimeters a second, and the last column of both tables shows the number of ants timed for each observation.

The measures were made in the same manner as previously for *L. apiculatum*, except that both *Tapinoma* and *Iridomyrmex* are valley ants and the colonies studied were located in Pasadena at an altitude of about one thousand feet. The accuracy of the measures is of the same order as before. The measures were made in 1920 on August 4, 5, and 6 for *Iridomyrmex* and on September 5 and 6 for *Tapinoma*. The stations for the former were on cement and humus. The observed colony of *Tapinoma*,

however, was running in a dense column through a room in which the temperature could be regulated with the aid of a gas-burning furnace. The artificial control of the heat began with the seventh observation. As the temperature became higher than the optimum, the ants refused to enter the room. Those already in the room at temperatures higher than 40° became erratic and sluggish, and no longer passed through the speed trap. Ants carrying burdens of food naturally showed the greatest willingness to follow the scent trails at high temperatures.

TABLE I

OBSERVATIONS OF *Tapinoma sessile* SAY

	OBS.	TIME	TEMP.	SPEED	NUMBER	OBS.	TIME	TEMP.	SPEED	NUMBER
T	1	7:38 A.M.	20°7	1.24	20	T 17	5:00 P.M.	38°9	2.66	7
	2	8:37	21.0	1.28	20	18	5:08	36.9	3.18	10
	3	10:42	21.9	1.44	20	19	5:16	35.8	3.22	20
	4	11:42	22.6	1.50	20	20	5:27	33.7	3.03	20
	5	12:27 P.M.	23.5	1.57	20	21	5:41	33.3	2.88	20
	6	2:01	25.2	1.67	20	22	5:48	32.6	2.84	15
	7	2:29	25.4	1.78	20	23	6:00	32.0	3.00	20
	8	2:37	28.0	2.12	20	24	6:40	30.2	2.45	20
	9	2:48	29.0	2.18	20	25	7:51	28 3	2.30	20
	10	2:57	30.7	2.66	20	26	8:10	27.9	2.27	20
	11	3:13	32.3	2.55	20	27	8:25	26.8	2.07	10
	12	3:40	34.7	2.94	20	28	9:12	26.0	1.92	10
	13	3:55	35.6	3.12	20	29	5:18 A.M.	20.2	0.99	20
	14	4:10	36.6	3.16	20	30	5:35	20.2	0.98	20
	15	4:24	37.2	3.13	17	31	6:38	19.7	0.95	20
	16	4:42	41.5	....	..					

TABLE II

OBSERVATIONS OF *Iridomyrmex humilis* MAYR

	OBS.	TIME	TEMP.	SPEED	NUMBER	OBS.	TIME	TEMP.	SPEED	NUMBER
I	1α	6:58 P.M.	29°4	3.49	20	I 12α	6:32 P.M.	30°0	3.37	20
	2α	7:06	28.2	3.10	18	13β	7:19	30.6	3.34	20
	3α	7:14	27.5	3.03	20	14β	7:48	29.3	3.17	20
	4α	8:20	25.6	2.62	24	15α	7:56	25.9	2.80	20
	5α	8:29	25.4	2.69	20	16α	8:04	25.2	2.62	20
	6β	5:37	33.5	4.46	20	17β	5:49	33.8	4.32	20
	7β	5:43	33.5	4.38	20	18β	5:56	33.8	4.34	20
	8β	5:51	33.3	4.18	20	19γ	6:09	30.4	3.76	20
	9β	6:12	33.0	4.17	20	20γ	6:16	30.4	3.56	20
	10β	6:20	33.1	4.03	20	21β	6:27	32.2	4.03	20
	11α	6:23	30.3	3.57	20					

At a given temperature the speed of *Iridomyrmex* is nearly fifty per cent greater than that of *Tapinoma*. The conspicuous difference in structural proportions between the two species probably accounts not only for the relative slowness of *Tapinoma*, but also for its lower optimum temperature.

The Argentine ants and the *Liometopa* are of very similar body proportions (length of legs relative to weight of body), and, as a result, the measures for *Iridomyrmex* fall closely along the curve already obtained for the *Liometopa* on Mount Wilson.

In figure 1, the upper curve shows the observations on *Tapinoma*, with temperature in degrees centigrade and speed in centimeters a second for ordinates and abscissas. Q_{10} is 2.4 at 25° and 1.7 at 30°. The highest speed is reached at 36°.

The lower curve in figure 1 refers to *Iridomyrmex* ants, which were systematically timed only throughout a temperature range of nine degrees. The dotted line through the observations is the empirical curve that represents the observations on *L. apiculatum*.

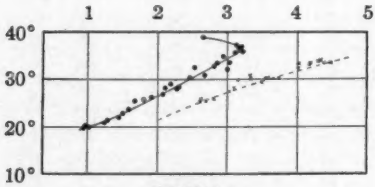

FIGURE 1
Speed curves for *Tapinoma sessile* and *Iridomyrmex humilis*.

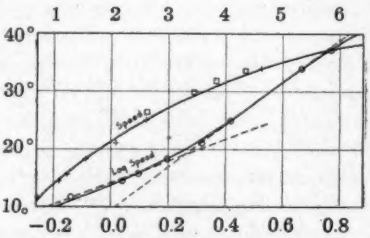

FIGURE 2
Speed curves for *Liometopum apiculatum*.

In figure 2 the mean results for *L. apiculatum* are plotted with temperatures as ordinates. The speeds in centimeters a second are abscissas for the upper curve and the logarithms of speed are abscissas for the lower curve. The observations, grouped into means of five, have been taken from the earlier paper, with the addition of a few unpublished measures (which have not affected the form of the original observational curve). The open squares on the upper curve represent the means of the observations on *Iridomyrmex* in table II above.

If Q_{10} is constant throughout any range of temperature, the logarithm of the speed should increase linearly throughout that interval and the observations should fall along a straight line. Between temperatures 22° and 35°, a value of log Q_{10} = 0.28 holds within the uncertainty of the measures, but above and below these limits the deviations are in the same direction as frequently found for physiological processes—as noted by Krogh,[2] for instance, for the rate of CO_2 production and of pupal development in *Tenebrio molitor*.

On the other hand, it appears, as shown in the figure, that two straight lines, corresponding to Q_{10} = 3.3 for temperatures below 20° and Q_{10} = 1.9 between 20° and 38°, represent fairly well the logarithms of the speed of *Liometopum*. If much weight could be attached to the apparent abrupt change from one constant Q_{10} to another, it would support Pütter's[3] thesis

of limiting factors (slow or counter-reactions) controlling the temperature coefficients of life processes.

Further consideration may be given to the question whether possibly two reactions (among the many involved in the running of ants) limit and control the resultant temperature coefficients. The van't Hoff-Arrhenius relation, $Q_{10} = e^{10A/T_1T_2}$ (where the temperatures are on the Kelvin scale, $T_2 = T_1 + 10°$, and $A = \mu/2$ can be taken as half the relevant heat change, in calories), may be written $\mu = T_2T_1 \log Q_{10}/5$ mod, or, to a sufficiently satisfactory approximation, $\mu = 0.46\ T_m^2 \log Q_{10}$, with $T_m = (T_2 + T_1)/2$.

Taking the values given above for *Liometopum*, that is, $Q_{10} = 3.3$ at $T_m = 288°$, and $Q_{10} = 1.9$ at $T_m = 302°$, we compute that the corresponding values of μ are 19,800 and 11,700.

Assuming that there is a distinct change in Q and in μ at about 20° C, and taking $\mu = 20{,}000$ for the lower temperatures and $\mu = 11{,}000$ for the higher (in agreement, for instance, with the values of the heat of dissociation experimentally derived by Volkmann[4] in a study of temperature coefficients in a number of purely chemical reactions), we compute the following values of Q_{10} from the relations $\log Q_{10} = 43{,}500/T_m^2$ and $\log Q_{10} = 24{,}000/T_m^2$, respectively:

T_m	COMPUTED Q_{10}	OBSERVED Q_{10}	DIFFERENCE
283°	3.5	3.9	+0.4
286	3.4	3.2	—0.2
289	3.3	2.8	—0.5
292	3.2	2.6	—0 6
—	—	—	—
295	1.9	2.0	+0.1
298	1.9	1.9	0.0
301	1.9	1.9	0.0
304	1.8	1.9	+0.1
307	1.8	1.9	+0.1
310	1.8	2.0	+0.2

The values of Q_{10} directly determined from the observations plotted logarithmically in figure 2 are given in the third column of the foregoing tabulation. The differences, O-C, in the last column show the deviation from the theoretical values.

The rapid change of the observed Q for lower temperatures does not strongly favor the hypothesis of a single abrupt change in μ. A constant value of μ at about 11,000, for temperatures from 20° C to 35° C, appears to be justified. But further observation is necessary to test the indicated variability of μ for temperatures below 20° C.

[1] Shapley, Harlow, these PROCEEDINGS, **6**, 1920 (204–211).

[2] Krogh, August, *Zeit. Allg. Physiol.*, **16**, 1914, pp. 163 and 178.

[3] Pütter, A., *Ibid.*, 1914 (574–627).

[4] Volkmann, *Dissertation*, Freiburg, i. B., 1908.